

Supplementary Information: Nanocrystals Self-Assembled in Superlattices Directed by the Solvent-Organic Capping Interaction

S1: Details about the molecular dynamic simulation model.

In the modeled nanocrystals (NCs) each interaction site might be thought of as being one ZrO_2 unit, but care should be taken about this interpretation as the size of each unit cell is much smaller than that which is experimentally observed for this NC. The reason for shrinking the unit cells is that a model NC with the experimental crystal structure became excessively soft and artifacts were detected, e.g., the non-physical diffusion of one NC into another (results not shown here).

The NCs was capped with Oleic acid (OA) being the molecules were modeled as a five-site chain, the polar head being bound to a NC surface site, followed by four apolar sites attached to each other, with a 120° kink between the second and the third apolar sites, mimicking the cis defect at the ninth carbon atom of oleic acid. As compared to the NCs described in the experimental section, this model NC is smaller and the oleic acid coverage is larger.

Nonetheless, our model captures the essential features of the physical system under investigation.

Two types of model systems were considered, one comprising one NC and 9999 solvent molecules, which represents the reference, non-assembled state of the NC in each solvent, and another 8-fold larger but with the same NC/solvent ratio, allowing NCs to interact with each other. The systems containing one NC were generated by placing both the NC and the solvent molecules at random positions in a cubic box with an edge length large enough to accommodate each solvent at its experimental density. Strong repulsive interactions were avoided in the initial

configuration by setting a cutoff distance as the acceptance criterion for the insertion of solvent molecules. Further relaxation of repulsive interactions was achieved by means of an energy minimization using the steepest descent method. The resulting structures had energy gradients smaller than $100 \text{ kJ mol}^{-1} \text{ nm}^{-1}$ for all sites in the model systems (Figure S.1). We performed the integration of the equations of motion using these optimized structure as the starting configurations, reaching a total integration time of 100 ns for each system. The final structures obtained after these one-NC simulations were replicated in all three directions, resulting in larger model systems with eight equally spaced NCs within a cubic box with either hexane or chloroform (Figure S.2). It should be noted that the replication procedure increased the number of solvent molecules by an 8-fold factor, so these larger systems still have the same composition as the one-NC systems. Thus, any new structural feature should be ascribed to the interaction between NCs and not to changes in composition. The equations of motion were integrated again taking these 8-NCs model systems as the starting configuration. Due to the increased complexity, it was necessary to perform a 100 ns-long relaxation run, followed by a 100 ns-long production run.

We have chosen to assemble model systems that were more concentrated than the colloidal dispersions that were employed in the experimental section, both because the smaller size reduces the computation demand and also because the more concentrated suspensions should be observed during the drying process of the solvent. Thus, our model systems are more representative of the self-assembling process taking place over the solid substrate as the solvents evaporated.

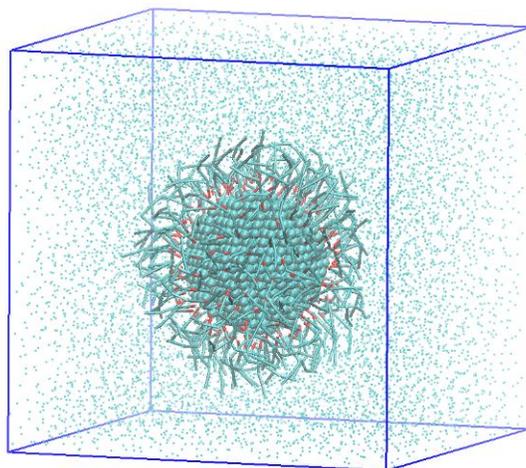


Figure S.1 – Initial structure for the system containing one NC and 9999 solvent molecules. NC sites are represented by van der Waals spheres whereas oleic acid molecules are drawn as cylinder segments for each site (the red portions are the polar headgroups).

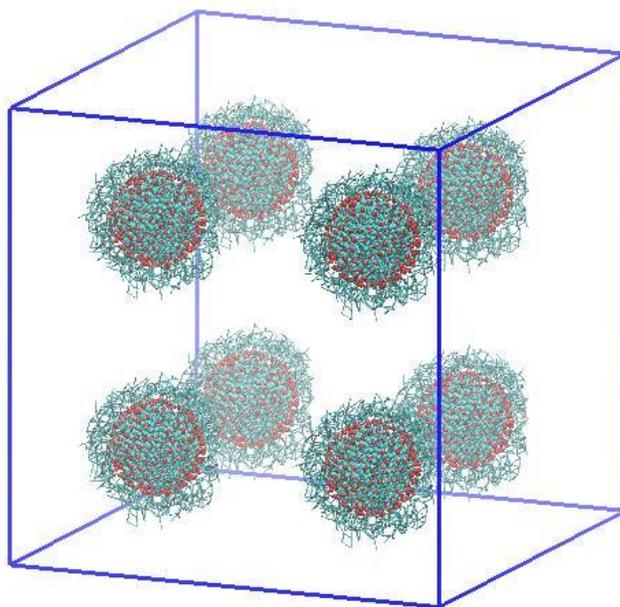


Figure S.2 – Initial structure for the system containing 8 NCs (solvent molecules are not shown for clarity).

S2: Synthesis of ZrO₂ directly in oleic acid.

The synthesis of ZrO₂ was performed directly in oleic acid using the follow procedure: In a glove box under controlled atmosphere, 120 mL of zirconium isopropoxide solution (0.25 molar) was prepared in oleic acid, in a glass reaction vessel. The solution was homogenized using magnetic stirring bar at 50°C. Then, vessel was removed from the glovebox and heated at 250°C during 48h in a closed stirred reactor system. After thermal treatment, the system was cooled to room temperature and the suspension was centrifuged to collect a white powder that was washed twice using acetone to remove all excess of oleic acid and byproducts. Then the material was analyzed by XRD and TEM.

The direct synthesis in oleic acid could avoid the ligand exchange. However, the crystalline phase and the morphology was not the same obtained in BA. The Figure S.3 show the XRD data for the sample synthesized in oleic acid, where the monoclinic phase was identified.

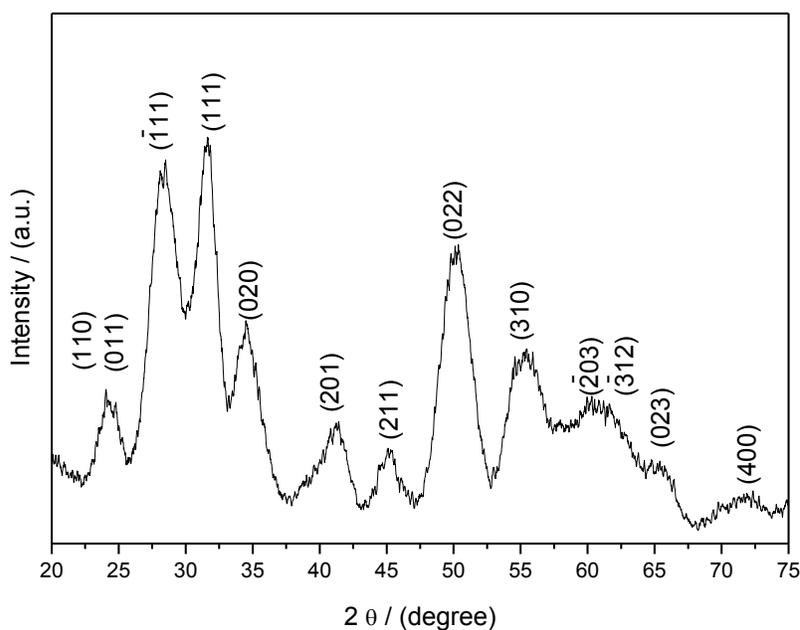


Figure S.3: X-ray diffraction for the ZrO₂ synthesized in oleic acid.

The material synthesized in oleic acid was analyzed by TEM. The Figure S.4a shows a low magnification HRTEM image of ZrO₂ NCs. Figure S.4b shows a high magnification HRTEM image. It is clear the formation of ZrO₂ nanocrystal with rods shape.

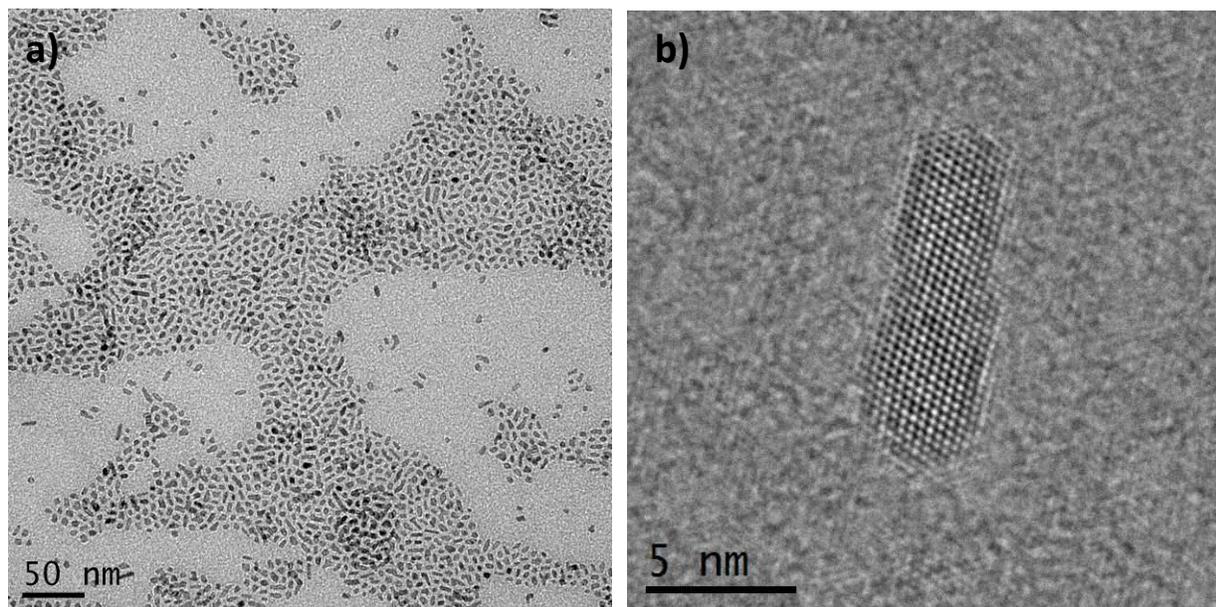


Figure S.4: TEM image for the ZrO₂ synthesized in OA. a) low magnification image for general visualization. b) HRTEM image of one ZrO₂ NC obtained in oleic acid.

S3: Organic solvent influence in the Self-Assembly

Solvents with different polarities were used to obtain NCs colloidal solutions. Those solution where used to prepare thin films in the TEM grids. The Figure S.5 shows single layer assemblies of ZrO₂ nanocrystals using the colloidal solutions with different solvents.

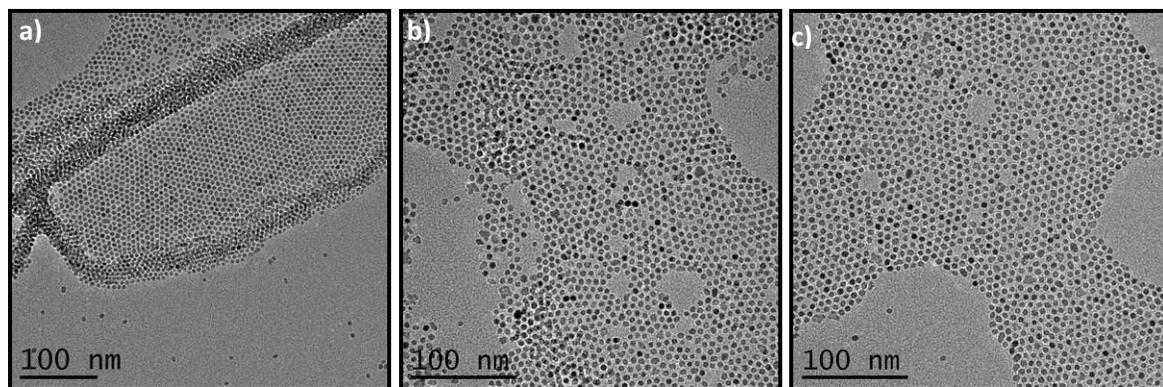


Figure S.5: Single layer assemblies of ZrO_2 nanocrystals using the colloidal solutions with different solvents. a) Chloroform; b) Toluene; c) Hexane.